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LOCAL SPIN-DENSITY CALCULATION FOR IRON: EFFECT OF SPIN INTERPOLATION ON GROUND STATE PROPERTIES

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Scalar relativistic self consistent linearized muffin-tin orbital (LMTO) calculations for bcc and fcc Fe have been performed with several different local approximations to the exchange and correlation energy density and potential. Overall, in contrast to the conclusions of previous studies, ~~we find that~~ the local spin density approximation (LSDA) to exchange and correlation can provide an adequate description of bulk Fe, provided a proper parameterization of the correlation energy density and potential of the homogeneous electron gas over both spin and density is used. Lattice constants, found from the position of the minimum of the total energy as a function of Wigner-Seitz radius, agree to within ~~1% (for s,p,d LMTOs only) and within~~ 1-2% (for s,p,d,f LMTOs) of the experimental lattice constants for all forms used for the local correlation. The best agreement, however, was obtained using a local correlation potential derived from the Vosko-Wilk-Nusair form for the spin dependence of the correlation energy density. The calculation performed with this correlation potential was also the only calculation to correctly predict a bcc ferromagnetic ground state. All the calculations gave satisfactory values for the magnetic moment, though the experimental bulk modulus was overestimated by more than 30%, a feature in agreement with most previously published calculations. The agreement in bulk modulus is comparable to that obtained in paramagnetic calculations; therefore we attribute this error not to a failure in the LSDA, but rather, this error is most likely a result to the atomic sphere approximation (ASA).

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Local Spin-Density Calculations for Iron: Effect of Spin Interpolation on Ground State Properties

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Scalar relativistic self consistent linearized muffin-tin orbital (LMTO) calculations for bcc and fcc Fe have been performed with several different local approximations to the exchange and correlation energy density and potential. Overall, in contrast to the conclusions of previous studies, we find that the local spin density approximation (LSDA) to exchange and correlation can provide an adequate description of bulk Fe, *provided* a proper parameterization of the correlation energy density and potential of the homogeneous electron gas over both spin and density is used. Lattice constants, found from the position of the minimum of the total energy as a function of Wigner-Seitz radius, agree to within 1% (for s,p,d LMTOs only) and within 1-2% (for s,p,d,f LMTOs) of the experimental lattice constants for all forms used for the local correlation. The best agreement, however, was obtained using a local correlation potential derived from the Vosko-Wilk-Nusair form for the spin dependence of the correlation energy density. The calculation performed with this correlation potential was also the only calculation to correctly predict a bcc

ferromagnetic ground state. All the calculations gave satisfactory values for the magnetic moment, though the experimental bulk modulus was overestimated by more than 30%, a feature in agreement with most previously published calculations. The agreement in bulk modulus is comparable to that obtained in paramagnetic calculations; therefore we attribute this error not to a failure in the LSDA, but rather, this error is most likely a result of the atomic sphere approximation (ASA).

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INTRODUCTION

Considerable success has been achieved by electronic structure calculations in the prediction of the ground state properties of non-magnetic bulk crystals. Lattice constants can usually be obtained to within $1 - 2\%$ or so of the experimental value;[1] elastic constants such as bulk moduli to within 0-30%.[1,2] Consistent results have been obtained using a variety of electronic structure techniques, including the linearized augmented plane wave approach (LAPW) (or its generalization to full potential, the FLAPW method[3]), Korringa-Kohn-Rostoker (KKR)[1], linearized muffin-tin orbital (LMTO)[4], full potential LMTO[5] and pseudopotential[6] approaches to name a few. All of these methods adopt the local density approximation (LDA) to the exchange-correlation energy and potential. There have been many forms suggested for the energy and potential functionals. The commonly used classes are: (1) the form suggested by Slater[7] ($X\alpha$) and the exchange only Kohn-Sham (KS)[8] form where the functional dependence on the density is of the simple $\rho^{\frac{1}{3}}$ form, (2) the fits to RPA based calculations by Hedin and Lundqvist (HL),[9] Gunnarsson, Lundqvist, and Wilkins (GLW),[10] and von Barth-Hedin (VBH);[11] and (3) the parameterization of the Monte Carlo data of Ceperley and Alder[12] by Perdew and Zunger (CA).[13] The latter is expected to be the best test of the LSDA, since it provides the most accurate description of the homogeneous electron gas.

Historically the LSDA has not had the same success in magnetic systems as the LDA has had in non-magnetic systems. The 3d transiti . metal Fe is a good example of a magnetic system which has been extensively studied, yet one which has been to date rather poorly described by LSDA-based band structure calculations. The structural and magnetic properties of Fe have been studied using the FLAPW method by Wang *et al.*,[14] Hathaway *et al.*,[15] and Jansen *et al.*[16] In these calculations, the authors find that the ground state crystal structure of Fe is non-magnetic fcc, that the bulk modulus is too

large and that the lattice constant is significantly too small. The original calculations of Kübler[17] also produced an incorrect ground state. More recent LMTO calculations by Bagno *et al.*[18] produced similar results to the FLAPW studies though a good bulk modulus was obtained, unlike any other LSDA calculation. The authors also considered the effects of various gradient terms (non-local corrections) where they found that they could indeed stabilize the ferromagnetic bcc phase and also expand the lattice constant. It is the purpose of this Rapid Communication to consider the sensitivity of the aforementioned ground state properties to changes in the form of spin dependence of the correlation effects, perhaps answering the questions of why previous LSDA calculations have given a poor ground state description and whether it is necessary to resort to non-local corrections.

All the LSDA calculations are based upon fits of the exchange-correlation energy density over the electron gas density (or equivalently, r_s) and spin polarization, ζ. The latter is usually approximated at intermediate ζ by an interpolation between the extreme paramagnetic ($\zeta = 0$) and ferromagnetic ($\zeta = 1$) limits using a formula suggested by von Barth and Hedin.[11] This scaling, while correct for the exchange part of the potential and energy in a homogeneous system, is not correct for the correlation contribution. Vosko *et al.*[19] (VWN) suggested an improved spin interpolation formula for the correlation energy, which successfully fits the CA data over the range of ζ to within 1 mRy, and it gives a significant improvement over the VBH interpolation. This interpolation for the correlation energy is of complex form, and the corresponding functional forms for the potentials are therefore also complex, since the potentials are derived from the functional derivatives of the energy. The equations for the correlation energy and potentials as a function of spin polarization are as follows:[20]

$$\epsilon_c(r_s, \zeta) = \epsilon_c^P(r_s) + \Delta\epsilon_c(r_s, \zeta) \tag{1}$$

where $\Delta\epsilon_c(r_s,\zeta)$ is expressed in terms of the spin stiffness α_c

$$\Delta\epsilon_c(r_s,\zeta) = \alpha_c(r_s)\frac{f(\zeta)}{f''(0)}[1 + \beta(r_s)\zeta^4] \tag{2}$$

and

$$\begin{aligned}\mu_c^{\uparrow(\downarrow)}(r_s,\zeta) = \mu_c^P + \Delta\epsilon_c + \frac{f(\zeta)}{f''(0)}\left[-\frac{r_s}{3}\frac{d\alpha_c(r_s)}{dr_s}\left(1+\beta(r_s)\zeta^4\right) + \alpha_c(r_s)\left(-\frac{r_s}{3}\frac{d\beta(r_s)}{dr_s}\zeta^4\right)\right] \\ \pm\frac{\alpha_c(r_s)}{f''(0)}\left[4\beta(r_s)\zeta^3 f(\zeta) + \left(1+\beta(r_s)\zeta^4\right)f'(\zeta)\right](1\mp\zeta)\end{aligned} \tag{3}$$

where

$$\beta(r_s) = \frac{f''(0)\Delta\epsilon_c(r_s,1)}{\alpha_c(r_s)} - 1, \tag{4}$$

$$\mu_c^P(r_s) = \epsilon_c^P(r_s) - \frac{r_s}{3}\frac{d\epsilon_c^P(r_s)}{dr_s}, \tag{5}$$

and

$$f(\zeta) = [(1+\zeta)^{\frac{4}{3}} + (1-\zeta)^{\frac{4}{3}} - 2]/(2^{\frac{4}{3}} - 2). \tag{6}$$

Vosko *et al.*[19] obtained the following expression for α_c

$$\begin{aligned}\alpha_c(r_s) = A_\alpha\Bigg(\ln\frac{r_s}{X(r_s)} + \frac{2b}{Q}\tan^{-1}\frac{Q}{2\sqrt{r_s}+b} - \frac{bx_0}{X(x_0^2)}[\ln\frac{(\sqrt{r_s}-x_0)^2}{X(r_s)} \\ + \frac{2(b+2x_0)}{Q}\tan^{-1}\frac{Q}{2\sqrt{r_s}+b}]\Bigg)\end{aligned} \tag{7}$$

where

$$X(r_s) = r_s + b\sqrt{r_s} + c; \qquad Q = \sqrt{4c - b^2} \tag{8}$$

and where appropriate parameters are given in Table 1. The derivative of α_c is given by

$$r_s\frac{d\alpha_c(r_s)}{dr_s} = A_\alpha\left(\frac{1 + b_1 r_s^{\frac{1}{2}}}{1 + b_1 r_s^{\frac{1}{2}} + b_2 r_s + b_3 r_s^{\frac{3}{2}}}\right) \tag{9}$$

where $b_1 = \frac{bx_0 - c}{cx_0}$, $b_2 = \frac{x_0 - b}{cx_0}$, and $b_3 = -\frac{1}{cx_0}$.

The derivative of β is given by

$$r_s\frac{d\beta(r_s)}{dr_s} = \frac{f''(0)}{\alpha_c(r_s)}r_s\frac{d\left(\epsilon_c^F(r_s) - \epsilon_c^P(r_s)\right)}{dr_s} - \frac{f''(0)\left(\epsilon_c^F(r_s) - \epsilon_c^P(r_s)\right)}{\alpha_c^2(r_s)}r_s\frac{d\alpha_c(r_s)}{dr_s}. \tag{10}$$

In the above, P denotes the paramagnetic limit and F the ferromagnetic limit. In these limits, we have used the Perdew-Zunger [13] parameterization:

$$\epsilon_c^i = \begin{cases} \frac{\gamma_i}{1+\beta_1^i\sqrt{r_s}+\beta_2^i r_s}, & r_s \geq 1 \\ A_i \ln r_s + B_i + C_i r_s \ln r_s + D_i r_s, & r_s < 1 \end{cases} \tag{11}$$

and

$$\mu_c^i = \begin{cases} \frac{\epsilon_c^i\left(1+\frac{7}{6}\beta_1^i\sqrt{r_s}+\frac{4}{3}\beta_2^i r_s\right)}{1+\beta_1^i\sqrt{r_s}+\beta_2^i r_s}, & r_s \geq 1 \\ A_i \ln r_s + (B_i - \frac{1}{3}A_i) + \frac{2}{3}C_i r_s \ln r_s + \frac{1}{3}(2D_i - C_i) r_s, & r_s < 1 \end{cases} \tag{12}$$

The VWN parameterization for ϵ_c^P and ϵ_c^F, which is distinct from the VWN spin interpolation, could have also been used. Although this makes comparison with other VWN results difficult, the difference between the two is less than 1% [19] over all physical ranges of r_s. The results here were intended to emphasize the sensitivity of ground state properties to the form of spin interpolation.

The values of the various parameters are given in table 2, and all energies are in Rydbergs.

The failure in previous calculations using the LSDA then could arise from either the breakdown of the LSDA itself or from the use of the VBH spin interpolation formula in obtaining the spin dependent correlation potential. We tested a number of parameterized LSDA functionals to see whether the relatively poor agreement with experiment obtained in previous calculations for magnetic systems compared to non-magnetic systems can be remedied by using another form for the spin dependent correlation potential.

CALCULATIONAL DETAILS

The calculations presented in this paper were performed with the scalar relativistic LMTO method, which used a fully relativistic frozen core. We have tested several different local density functionals: namely the VBH, CA, KS, and GLW forms with the VBH spin interpolation and the CA with the VWN interpolation. We found that for all the functionals tested (CA, VBH, and GLW) that the bcc ferromagnetic phase had a lower total energy than the corresponding non-magnetic bcc phase, though we did not test the stability of antiferromagnetic fcc phase relative to the non-magnetic phase. Care was taken both to converge the total energies to 6 decimal places and to sample the region around the minimum densely so that the lattice constant, magnetic moment, and particularly the bulk modulus could be accurately determined. The number of k points used in the Brillouin zone integration was systematically increased until convergence was achieved. The tetrahedron method was employed for this integration with convergence typically achieved by 500 k points. LMTO calculations with s,p, and d as well as s,p,d, and f LMTOs have been examined. For non-magnetic fcc Fe and ferromagnetic bcc Fe, we summarize the results of calculations based on l=3 with about 500 k points for the CA and VBH functionals only. The same trends were also observed in the l=2 calculations; the addition of the f LMTO contracted the lattice and reduced the moment slightly. The details and approximations behind the LMTO approach have been discussed in detail in other works, and we refer the reader to reference 4 for an excellent discussion of this.

RESULTS

Figure 1 shows results of the energy versus Wigner-Seitz radius for non-magnetic fcc Fe obtained using the VBH and CA density functionals respectively for 525 k points. The total energy plotted excludes terms from the frozen core. Since we are always interested in energy differences, this constant will not be important. Figure 2 shows calculations with 506 k points for ferromagnetic bcc Fe with the VBH functional and the CA functional using both the VBH and VWN spin interpolation formulae. The results for lattice constant, magnetic moment, bulk modulus, and stable ground state crystal structure are given in table 3. We see that lattice constants are within 2%, magnetic moments within 5%, and bulk moduli are too high by 30-40%. The errors in bulk moduli are comparable to those obtained in paramagnetic LMTO calculations for the 3d transition metals. The bulk modulus is extremely sensitive to the curvature of the total energy curve, and errors associated with the LMTO approximation aside from LSDA could easily account for this discrepancy. Work to elucidate the source of error is at present underway using the full potential LMTO method.[21] The magnetic moment is slightly underestimated. This is a result of the Wigner-Seitz sphere approximation which will tend to overestimate the contribution from the antiferromagnetically polarized interstitial region. The significant *success* of the new parameterized correlation potential functional lies in the correct prediction of a ferromagnetic bcc ground state – a feature not observed in those functionals which use the VBH form of spin interpolation. The improved VWN spin interpolation in the correlation potential is consequently important for an accurate description of the magnetism.

CONCLUSIONS

Our results show that Fe has a sufficient sensitivity to correlation that the low lying states can reorder with the application of different spin interpolation forms. We used the spin interpolation formula of Vosko *et al.*[19] for the correlation energy density to provide accurate parameterized correlation potentials within the LSDA. The VWN spin interpolated correlation potential significantly improves the LSD description of ferromagnetic bcc Fe. While the calculations performed utilized the ASA, we believe that the trends will persist in a full-potential calculation, since the volume of space containing intermediate spin polarizations will be roughly the same. We conclude that a good description of the magnetic properties of bcc Fe is obtainable within the LSDA, provided the proper interpolation is used for both the correlation energy density and potential.

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Table 1

Parameters for VWN interpolation formula

parameter	value
A_α	$-1/3\pi^2$
C_α	$[\ln(16\pi/\alpha) - 3 + 0.531504]/3\pi^2$
b	1.13107
c	13.0045
x_0	-0.00475840
α	$(\frac{4}{9\pi})^{\frac{1}{3}}$

Table 2
Parameters for CA LSDA

parameter	Paramagnetic	Ferromagnetic
γ	-0.1423	-0.0843
β_1	1.0529	1.3981
β_2	0.3334	0.2611
A	0.0311	0.01555
B	-0.048	-0.0269
C	0.0020	0.0007
D	-0.0116	-0.0048

Table 3

Summary of LMTO local spin density calculations for bcc Fe.

LDA	spin interpolation	lattice constant (a.u.)	Magnetic Moment (μ_B)	Bulk Modulus (Mbar)	ground state
CA	VWN	5.3111	1.98	2.45	bcc
CA	VBH	5.3706	1.85	2.53	fcc
VBH	VBH	5.2941	2.12	2.52	fcc
experiment		5.4169[a]	2.12	1.68-1.73	bcc

[a] Reference 22.

Table 4

Summary of minimum total energy for the ferromagnetic bcc and paramagnetic fcc calculations.

LDA	spin interpolation	Crystal Structure	Energy (Ry)
CA		fcc	-44.2974
CA	VWN	bcc	-44.2993
CA	VBH	bcc	-44.2945
VBH	VBH	fcc	-44.5952
VBH	VBH	bcc	-44.5938

Figure Captions

Figure 1. Total energy (minus the frozen core term) versus Wigner-Seitz radius for paramagnetic fcc Fe: (a) CA LDA, and (b) VBH LDA.

Figure 2. Total energy (minus the frozen core term) versus Wigner-Seitz radius for ferromagnetic bcc Fe: (a) CA LDSA with VWN spin interpolation, (b) CA LDSA with VBH spin interpolation, and (c) VBH LDSA with VBH spin interpolation.

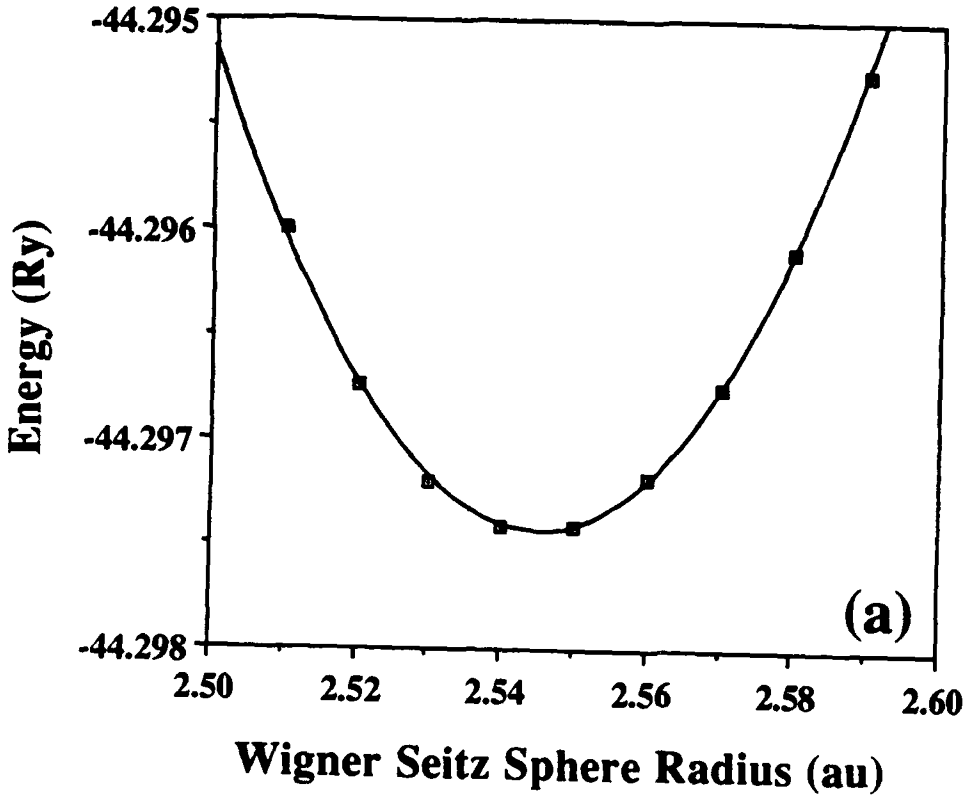

Figure 1a

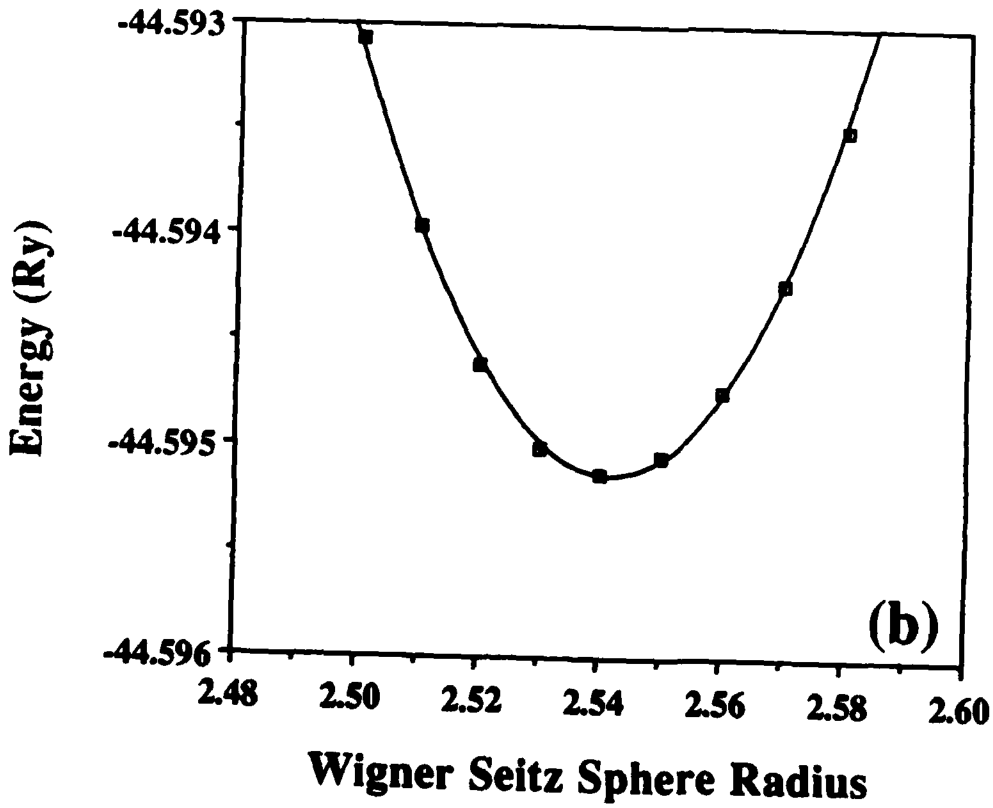

Figure 1b

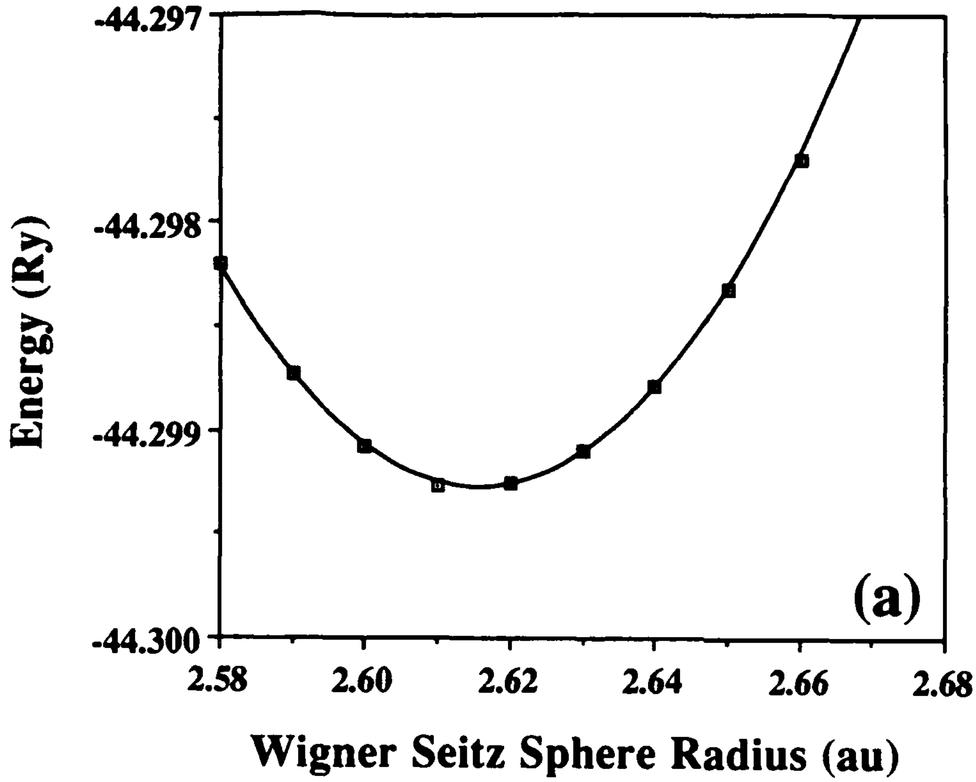

Figure 2a

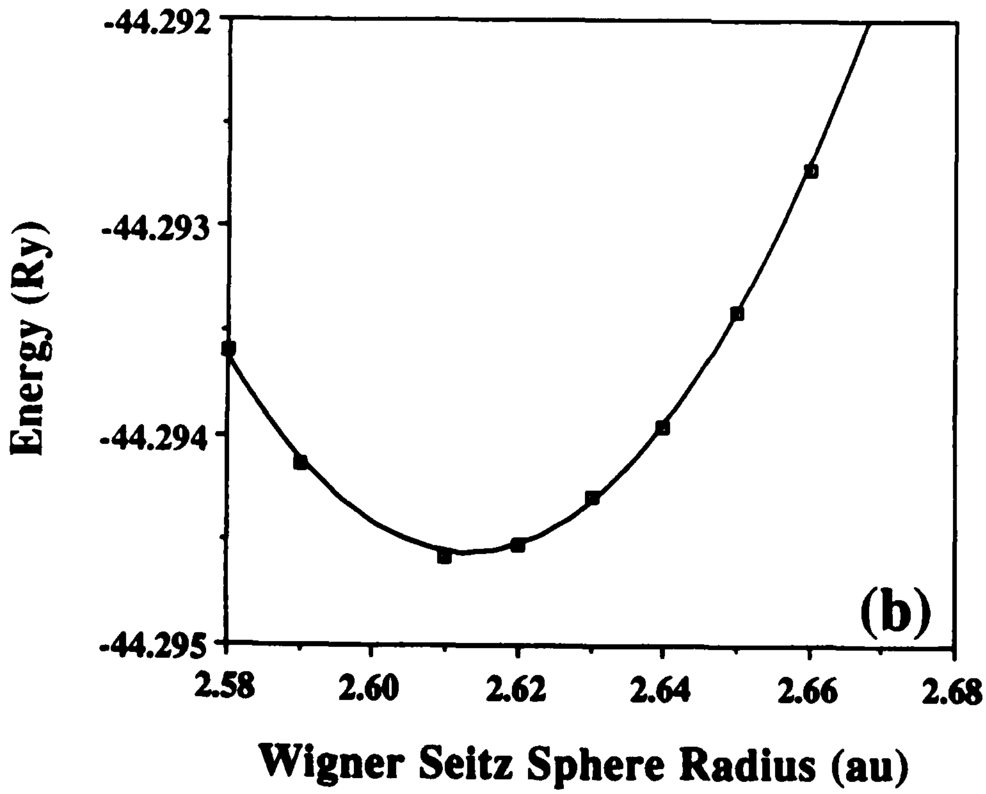

Figure 2b

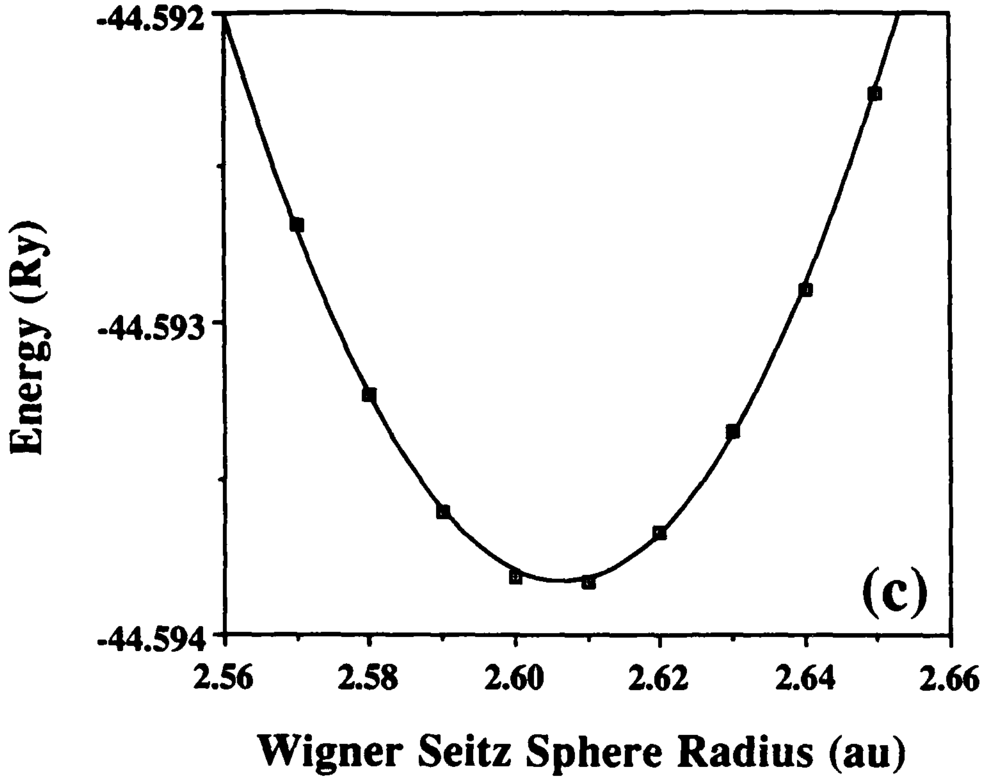
-44.592
-44.593
-44.594
Energy (Ry)
2.56
2.58
2.60
2.62
2.64
2.66
Wigner Seitz Sphere Radius (au)
(c)

Figure 2c